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# Synthesis, Characterization, and Some Chemical Properties of Unusual 16-Electron Dialkyl($\eta^5$-cyclopentadienyl)nitrosylmolybdenum and -tungsten Complexes[1]

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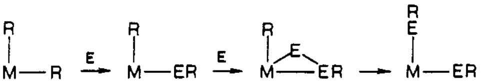
Novel 16-electron dialkyl complexes of molybdenum and tungsten, $CpM(NO)R_2$ [(Cp = $\eta^5$-$C_5H_5$; M = Mo or W; R = $CH_2SiMe_3$, $CH_2CMe_3$, $CH_2CMe_2Ph$, or $CH_2Ph$], result in high yields from the sequential treatment of $[CpM(NO)I_2]_2$ first with a Grignard reagent, RMgCl, and then water. When R = $CH_2SiMe_3$, the intermediate complexes $[CpM(NO)R_2]_2MgI_2{\cdot}Et_2O$ are isolable as red crystalline solids prior to the addition of $H_2O$. The final $CpM(NO)R_2$ compounds possess monomeric, piano-stool molecular structures, a fact that has been established for $CpW(NO)(CH_2SiMe_3)_2$ in the solid state by a single-crystal, X-ray crystallographic analysis. This compound crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions $a$ = 12.070 (2) Å, $b$ = 12.4360 (7) Å, $c$ = 13.5742 (15) Å, and $\beta$ = 104.856 (6)°. The most chemically interesting feature of the molecular structure involves the essentially linear (169.5 (6)°) WNO group in which the short W-N (1.757 (8) Å) and long N-O (1.226 (10) Å) bond lengths indicate the existence of considerable W→NO back-bonding. Consistently, the IR spectra of all the $CpM(NO)R_2$ complexes as Nujol mulls exhibit single, strong $\nu_{NO}$'s in the relatively low-energy range of 1540–1587 $cm^{-1}$. The chemical properties of these dialkyl compounds are exemplified by the reactions of $CpW(NO)(CH_2SiMe_3)_2$ with various substrates. Thus, this complex incorporates small Lewis bases such as $PMe_3$ directly at the tungsten center, 1:1 adducts resulting. Other Lewis base adducts undergo subsequent intramolecular transformations involving one of the alkyl groups. Hence, reaction of $CpW(NO)(CH_2SiMe_3)_2$ with *t*-BuNC affords the insertion product $CpW(NO)(CH_2SiMe_3)[\eta^2\text{-}C(CH_2SiMe_3){=}N\text{-}t\text{-}Bu]$ in 94% isolated yield. [Hydrolysis of this iminoacyl complex cleanly produces the corresponding methyl derivative, $CpW(NO)(CH_2SiMe_3)[\eta^2\text{-}C(CH_3){=}N\text{-}t\text{-}Bu]$.] Similarly, treatment of the tungsten dialkyl complex in hexanes with NO gas affords quantitatively the *N*-alkyl-*N*-nitrosohydroxylaminato compound $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}O_2N_2\{CH_2SiMe_3\})$, which exists in nonpolar solvents as a mixture of two isomers. Finally, reaction of $CpW(NO)(CH_2SiMe_3)_2$ with elemental sulfur or selenium results in the occurrence of the unprecedented sequential transformations



where M = CpW(NO), R = $CH_2SiMe_3$, and E = S or Se. When E = S, all three product complexes are isolable as analytically pure solids, but when E = Se, only $CpW(NO)(CH_2SiMe_3)(SeCH_2SiMe_3)$ and $CpW(NO)(SeCH_2SiMe_3)_2$ may be so obtained. All new complexes isolated during this investigation have been fully characterized by conventional spectroscopic methods.

Alkyl derivatives of transition metals are important reagents or intermediates in many stoichiometric and catalytic reactions.[3] However, the stabilities and reactivities of these complexes vary considerably, being markedly influenced by the natures of both the metal and the other ligands present.[3] In this latter regard, relatively little is known at present about how the physical and chemical properties of transition-metal–carbon $\sigma$-bonds are affected by the presence of nitrosyl ligands in the metal's coordination sphere. The most common types of alkyl nitrosyl complexes are those also containing $\eta^5$-cyclopentadienyl ligands (i.e. $\eta^5$-$C_5H_5$ (Cp) or $\eta^5$-$C_5Me_5$ (Cp*)).[4] Thus, compounds such as $CpM(NO)_2R$ (R = alkyl; M = Cr, Mo, or W),[5] $CpRe(CO)(NO)R$,[6] $Cp'Fe(NO)R_2$ (Cp' = Cp[7a] or Cp*[7b]), $Cp^*Ru(NO)R_2$,[8] and $CpCo(NO)R$[9] have been synthesized and fully characterized by conventional methods. Most interesting is the fact that the chemistry of these latter compounds has exhibited considerable variety. For instance, transformations (1)–(3) involving one or another of these complexes have been recently documented: (1) intermolecular insertion of electrophiles into the metal–carbon $\sigma$-bonds, e.g.[10]

$$CpCr(NO)_2R + NX^+ \xrightarrow{CH_2Cl_2} [CpCr(NO)_2\{N(X)R\}]^+ \quad (1)$$

where X = O, S, or $NC_6H_4NO_2$; (2) intramolecular insertion of bound NO into the metal–carbon $\sigma$-bonds, e.g.[9]

$$CpCo(NO)R \xrightarrow{THF} CpCo\{N(O)R\} \xrightarrow{+PPh_3} CpCo\{N(O)R\}(PPh_3) \quad (2)$$

(3) reductive elimination of coupled organic products, e.g.[7b]

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$$Cp^*Fe(NO)R_2 \xrightarrow{\Delta} [Cp^*Fe(\mu\text{-}NO)]_2 + R\text{–}R \qquad (3)$$

Not surprisingly, no one cyclopentadienyl alkyl nitrosyl complex is yet known to exhibit all three of the reactivity patterns (1)–(3).

Our recent research efforts have been directed at ascertaining the effects exerted by the CpM(NO) groups (M = Cr, Mo, or W) on their ancillary hydrocarbon ligands. To date, we have demonstrated that the CpMo(NO) fragment prefers to bind acyclic, conjugated dienes in a twisted, transoidal fashion,[11] an unprecedented feature that leads to the bound dienes exhibiting novel reactivities toward representative nucleophiles and electrophiles.[12] In this paper, we wish to report the effects that the CpM(NO) (M = Mo or W) groups have on alkyl ligands by describing in detail the synthesis, characterization, and some chemistry of various $CpM(NO)R_2$ complexes. These remarkable compounds are formal 16-electron species whose reactivity patterns are yet again different from those outlined in (1)–(3) above. Particularly noteworthy are the reactions of these coordinatively unsaturated species with small molecules such as $O_2$, $S_8$, and $Se_8$ which afford unprecedented products. Portions of this work have been previously communicated.[13]

## Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. General procedures routinely employed in these laboratories have been described in detail previously.[14] The reagents $[CpMo(NO)I_2]_2$,[15] $[CpW(NO)I_2]_2$,[16] $Me_3SiCH_2MgCl$,[17] $PMe_3$,[18] red Se,[19] and *t*-BuNC[20] were prepared by the published procedures. All other reagents were purchased from commercial suppliers and were used without further purification.

**Preparation of the Complexes $[CpM(NO)(CH_2SiMe_3)_2]_2MgI_2{\cdot}Et_2O$ (M = Mo, 1b; M = W, 1a).** Both complexes were synthesized in a similar manner. The experimental procedure, using the tungsten complex as a representative example, was as follows.

To a red-purple, stirred suspension of $[CpW(NO)I_2]_2$ (25.0 g, 23.5 mmol) in $Et_2O$ (500 mL) at 0 °C was added dropwise an $Et_2O$ solution of $Me_3SiCH_2MgCl$ (0.76 M, 124 mL, 94.2 mmol). The supernatant solution gradually became red in color as the quantity of insoluble solid diminished. The mixture was stirred for 30 min to ensure completion of the reaction and was then centrifuged to remove traces of insoluble matter. The supernatant solution was removed and cooled at 0 °C for 12 h[21] whereupon large red prisms of the desired product crystallized. The crystals were collected by filtration, washed with cold $Et_2O$ (2 × 25 mL), and dried at 20 °C in vacuo ($5 \times 10^{-3}$ Torr) for 3–4 h to obtain 22.0 g (76.6% yield) of $[CpW(NO)(CH_2SiMe_3)_2]_2MgI_2{\cdot}Et_2O$ (**1a**).

Starting with $[CpMo(NO)I_2]_2$, the analogous product complex $[CpMo(NO)(CH_2SiMe_3)_2]_2MgI_2{\cdot}Et_2O$ (**1b**) was isolated as a red, crystalline solid in comparable yield.

The formulations of both complexes are based on partial X-ray crystallographic analyses of single crystals of **1a** and **1b** which show them to be isostructural.[22] Furthermore, the $^1H$ and $^{13}C$ NMR spectra of these compounds (Table II) confirm the presence of one molecule of $Et_2O$ per molecule of the compound. Nevertheless, elemental analyses of different batches of **1a** and **1b** showed small variations in carbon and iodine contents consistent with the partial loss of the $Et_2O$ of solvation during workup and the occurrence of some Cl for I exchange prior to crystallization.

The mass spectral, analytical, IR, and NMR data for these and the other new complexes isolated during this work are gathered in Tables I–III.

**Preparation of the Complexes $CpM(NO)R_2$ (2; M = Mo or W; R = $CH_2SiMe_3$, $CH_2CMe_3$, $CH_2CMe_2Ph$, or $CH_2Ph$).** Again, all complexes were synthesized in a similar manner. The experimental procedure, using $CpW(NO)(CH_2SiMe_3)_2$ as a representative example, was as follows.

A vigorously stirred, red solution of **1a** (25.0 g, 20.5 mmol) in $Et_2O$ (500 mL) at room temperature was treated dropwise with an excess (~5 mL) of distilled and deaerated $H_2O$. A white solid began to precipitate immediately, and the supernatant solution gradually became violet as the mixture was stirred for 1 h. The volume of the mixture was then reduced to 300 mL under vacuum, and it was filtered through a Florisil column (3 × 20 cm) supported on a medium-porosity glass frit. The column was washed with $Et_2O$ (150 mL), and the combined filtrates were taken to dryness in vacuo. Crystallization of the remaining residue from hexanes at 0 °C afforded 15.1 g (81% yield based on tungsten) of $CpW(NO)(CH_2SiMe_3)_2$ (**2a**) as analytically pure, violet-purple crystals.

The analogous molybdenum compound $CpMo(NO)(CH_2SiMe_3)_2$ (**2b**) was obtained from **1b** in 61% isolated yield. However, in order to achieve this yield, shorter reaction times (i.e. 5–10 min), filtration through only a medium-porosity glass frit and rigorously oxygen-free conditions were mandatory.

The other dialkyl complexes $CpW(NO)(CH_2CMe_3)_2$ (**2c**), $CpW(NO)(CH_2CMe_2Ph)_2$ (**2d**), and $CpW(NO)(CH_2Ph)_2$ (**2e**) were obtained in 35–55% yields by employing similar procedures. In these three cases, however, the initial reaction of $[CpW(NO)I_2]_2$ with the appropriate Grignard reagent in $Et_2O$ produced a yellow precipitate rather than a red solution as in the cases having R = $CH_2SiMe_3$. Nevertheless, treatment of this precipitate in $Et_2O$ with $H_2O$ in the customary manner did produce the desired dialkyl complexes that were isolated as described above.

**Preparation of $CpW(NO)(CH_2SiMe_3)_2(PMe_3)$ (3).** To a stirred, violet solution of **2a** (0.906 g, 2.00 mmol) in hexanes (50 mL) at 0 °C was added dropwise an excess of $PMe_3$ (0.3 mL, 3 mmol). Yellow microcrystals began to precipitate immediately, but the mixture was kept overnight at −25 °C to complete the precipitation. The precipitate was collected the next day by filtration, washed with hexanes at 0 °C (2 × 15 mL), and dried at 0 °C and $5 \times 10^{-3}$ Torr for 4 h to obtain 0.97 g (92% yield) of $CpW(NO)(CH_2SiMe_3)_2(PMe_3)$ (**3**) as a yellow, crystalline solid. This solid can be recrystallized essentially quantitatively from $Et_2O$ at −15 °C in a closed system (to avoid loss of $PMe_3$).

$^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ −15.0 (s, $^1J_{^{31}P-^{183}W}$ = 157 Hz, $PMe_3$). Other physical data for this complex are contained in Tables I and III.

**Preparation of the Complexes $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}CR{=}NCMe_3)$ (R = $CH_2SiMe_3$, 4a; R = Me, 4b).**

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[21] Cooling this solution for longer periods of time results in the codeposition of white crystals of magnesium halides.

[22] Crystals of **1a** are tetragonal with $a$ = 16.3686 (9) Å, $c$ = 9.0927 (6) Å, $V$ = 2436.2 (2) Å$^3$, $Z$ = 2, and space group $P\bar{4}2_1m$. Only the W, I, Si, Mg, and the nitrosyl N and O atoms could be located. As a result of severe and unresolvable disorder, combined with relatively high thermal motion, the ether O atom and all carbon atoms could not be positioned. Nevertheless, the partial structure obtained does confirm the 2:1 adduct formulation invoked for this compound. With the W and I atoms anisotropic and the Si, Mg, N, and O atoms isotropic, the $R$ value is 0.112 for 867 reflections having $I \geq 3\sigma(I)$. The molybdenum analogue **1b** is isomorphous and isostructural: $a$ = 16.4243 (9) Å, $c$ = 9.0729 (8) Å, $V$ = 2447.5 (2) Å, $R$ = 0.161 for 738 reflections based on Mo, I, Si, Mg, N, and O. Both complexes **1a** and **1b** possess crystallographic $mm2$ ($C_{2v}$) symmetry (see Figure 1).

**Table I. Mass Spectral, Analytical, and IR Data for the Complexes**

| complex | mass spectra,[a] highest $m/z$ | anal. |  |  | IR (cm$^{-1}$) |  |  |
|---|---|---|---|---|---|---|---|
|  |  | C | H | N | $\nu_{NO}$ (Nujol mull) | $\nu_{NO}$ (soln) | $\nu_{other}$ (Nujol) |
| $[CpW(NO)(CH_2SiMe_3)_2]_2MgI_2 \cdot Et_2O$ (**1a**) | 453 | variable (see text) |  |  | 1505 | 1506[b] |  |
| $[CpMo(NO)(CH_2SiMe_3)_2]_2MgI_2 \cdot Et_2O$ (**1b**) | 367 | variable (see text) |  |  | 1520 | 1510[b] |  |
| $CpW(NO)(CH_2SiMe_3)_2$ (**2a**) | 453 | 34.43 (34.50) | 5.96 (6.00) | 3.09 (3.05) | 1541 | 1603[c] |  |
| $CpMo(NO)(CH_2SiMe_3)_2$ (**2b**) | 367 | 42.63 (42.73) | 7.38 (7.39) | 4.00 (3.83) | 1587 | 1625[c] |  |
| $CpW(NO)(CH_2CMe_3)_2$ (**2c**) | 421 | 42.47 (42.75) | 6.37 (6.41) | 3.20 (3.32) | 1560 | 1605[c] |  |
| $CpW(NO)(CH_2CMe_2Ph)_2$ (**2d**) | 545 | 55.29 (55.04) | 4.50 (4.77) | 2.39 (2.56) | 1540 | 1597[c] |  |
| $CpW(NO)(CH_2Ph)_2$ (**2e**) | 461 | 49.31 (49.48) | 4.09 (4.15) | 2.93 (3.04) | 1570 | 1601[c] |  |
| $CpW(NO)(CH_2SiMe_3)_2(PMe_3)$ (**3**) | 453 | 36.29 (36.29) | 6.70 (6.80) | 2.78 (2.64) | 1520 | 1560[b] | $\nu_{PMe_3}$ 950 |
| $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}C(CH_2SiMe_3){=}N(CME_3))$ (**4a**) |  | 40.07 (40.29) | 6.49 (6.71) | 5.55 (5.22) | 1530 |  | $\nu_{CN}$ 1685 |
| $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}C(CH_3){=}N(CMe_3)$ (**4b**) |  | 39.00 (38.82) | 6.00 (6.03) | 6.00 (6.03) | 1520 |  | $\nu_{CN}$ 1710 |
| $Cp(W)(NO)(CH_2SiMe_3)[\eta^2\text{-}O_2N_2(CH_2SiMe_3)]$ (**5**) | 513 | 30.48 (30.40) | 5.33 (5.26) | 8.18 (8.18) | 1581 | 1612[c] | $\nu_{O_2N_2R^1}$ 1247, 1192 |
| $CpW(NO)(CH_2SiMe_3)(SCH_2SiMe_3)$ (**6a**) | 485 | 32.14 (32.16) | 5.66 (5.56) | 2.98 (2.88) | 1575 | 1619[c] |  |
| $CpW(NO)(CH_2SiMe_3)(SeCH_2SiMe_3)$ (**6b**) | 532 | 29.39 (29.32) | 5.00 (5.07) | 2.61 (2.63) | 1575 | 1620[c] |  |
| $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}S_2CH_2SiMe_3)$ (**7**) | 517 | 30.51 (30.17) | 5.37 (5.22) | 2.66 (2.70) | 1560 | 1599[c] |  |
| $CpW(NO)(SCH_2SiMe_3)_2$ (**8a**) | 517 | 30.69 (30.17) | 5.39 (5.22) | 2.65 (2.70) | 1610 | 1645[c] |  |
| $CpW(NO)(SeCH_2SiMe_3)_2$ (**8b**) | 611 | 25.48 (25.53) | 4.37 (4.41) | 2.31 (2.29) | 1610 | 1647[c] |  |

[a] Probe temperatures 100–130 °C. [b] In benzene. [c] In hexanes.

**Table II. NMR Data for Complexes 1 and 2 in $C_6D_6$**

|  | $^1H$ NMR $\delta$ ($^2J_{^1H_A-^1H_B}$, Hz) |  |  |  | $^{13}C\{^1H\}$ NMR $\delta$ ($^1J_{^{13}C-^{183}W}$, Hz) |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | $C_5H_5$ | $CH_ACH_B$ | $CH_3$ | $C_6H_5$ | $C_5H_5$ | $CH_2$ | $CH_3$ | $C(CH_3)$ | $C_6H_5$ |
| **1a**[a] | 5.80 (s) | 2.16 (d), 0.06 (d) ($J$ = 8.3) | 0.30 (s) |  | 105.09 | 67.83 ($J$ = 81.7) | 2.67 |  |  |
| **1b**[a] | 5.41 (s) | 3.06 (d), 0.08 (d) ($J$ = 8.3) | 0.32 (s) |  | 103.82 | 71.42 | 2.29 |  |  |
| **2a** | 5.27 (s) | 2.31 (d), −0.52 (d) ($J$ = 8.3) | 0.30 (s) |  | 101.69 | 60.78 ($J$ = 83.1) | 2.85 |  |  |
| **2b** | 5.16 (s) | 3.09 (d), −0.26 (d), ($J$ = 8.3) | 0.33 (s) |  | 101.36 | 65.96 | 2.37 |  |  |
| **2c** | 5.14 (s) | 3.66 (d), −1.48 (d) ($J$ = 11.2) | 1.34 (s) |  | 101.23 | 91.53 ($J$ = 89.9) | 34.21 | 39.34 |  |
| **2d** | 4.75 (s) | 3.61 (d), −1.02 (d) ($J$ = 10.9) | 1.74 (s), 1.70 (s) | 7.43 (d), 7.24 (t), 7.09 (t) | 101.37 | 93.80 ($J$ = 92.8) | 33.29, 32.50 | 45.95 | 128.28, 125.98, 125.58 |
| **2e**[b] | 5.33 (s) | 2.15 (d), 1.15 (d) ($J$ = 7.8) |  | 7.26 (t), 6.93 (t), 6.75 (d) | 100.00 | 32.97 ($J$ = 59.0) |  |  | 130,40, 128.62, 127.66 |

[a] Spectrum also exhibits the signals characteristic of free $Et_2O$, i.e.: $^1H$ NMR $\delta$ 3.36 (q), 1.15 (t); $^{13}C\{^1H\}$ NMR $\delta$ 65.91, 15.36. [b] NMR data in $CD_2Cl_2$.

Neat *t*-BuNC (0.17 mL, 1.5 mmol) was added to a stirred solution of **2a** (0.453 g, 1.00 mmol) in THF (40 mL) at −78 °C. During the addition, the initially purple solution became yellow. The final mixture was permitted to warm to room temperature during 1 h and was then taken to dryness in vacuo. Crystallization of the remaining residue from $Et_2O$ at −15 °C afforded 0.51 g (94% yield) of $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}C\{CH_2SiMe_3\}{=}NCMe_3)$ (**4a**) as pale yellow crystals which were collected by filtration.

The related complex $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}C\{CH_3\}{=}NCMe_3)$ (**4b**) was obtained by employing the same procedure as outlined in the preceding paragraph but by using wet THF or by adding $H_2O$ to **4a** in THF. In either case, **4b** was isolated in virtually quantitative yield as a yellow, crystalline solid.

**Preparation of $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}O_2N_2\{CH_2SiMe_3\})$ (5).** Nitric oxide was slowly bubbled through a stirred solution of **2a** (0.91 g, 2.0 mmol) in hexanes (50 mL) at room temperature until the color of the solution changed completely from violet to pale yellow (~10 min). Volatiles were then removed from the final reaction mixture in vacuo, and the remaining residue was crystallized from 1:1 hexanes/ether at −15 °C to obtain 0.99 g (96% yield) of $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}O_2N_2\{CH_2SiMe_3\})$ (**5**) as large yellow crystals.

**Preparation of the Complexes $CpW(NO)(CH_2SiMe_3)(ECH_2SiMe_3)$ (E = S, 6a; E = Se, 6b).** To a stirred violet solution of **2a** (0.09 g, 0.2 mmol) in toluene (20 mL) at ambient temperature was added elemental sulfur (0.006 g, 0.2 mmol) to obtain a heterogeneous mixture. As this mixture was stirred for 16 h, the yellow sulfur slowly dissolved and the supernatant solution became red-violet in color. The final reaction mixture consisted of a clear, red-violet solution. Removal of solvent in vacuo and crystallization of the remaining residue from hexanes (10 mL) at −15 °C afforded $CpW(NO)(CH_2SiMe_3)(SCH_2SiMe_3)$ (**6a**) as analytically pure, red-violet crystals (0.08 g, 85% yield), mp 74 °C dec.

If red selenium was used in place of yellow sulfur in the above procedure, the related complex $CpW(NO)(CH_2SiMe_3)(SeCH_2SiMe_3)$ (**6b**) was obtained as red crystals in 83% yield in an analogous manner.

**Preparation of $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}S_2CH_2SiMe_3)$ (7).** A heterogeneous mixture of **2a** (0.09 g, 0.2 mmol) and elemental sulfur (0.013 g, 0.40 mmol) in THF (20 mL) was stirred at room temperature. The progress of the reaction was monitored by IR spectroscopy of the supernatant solution which was initially violet in color. After 2 h, the solution was red-violet and exhibited $\nu_{NO}$'s at 1600, 1590, and 1583 cm$^{-1}$. After 4 h, the absorption at 1583 cm$^{-1}$ due to **2a** had disappeared. During the next 10 h the band at 1600 cm$^{-1}$ due to **6a** gradually diminished in intensity while that at 1590 cm$^{-1}$ concomitantly increased in intensity. During this time the sulfur also gradually dissolved, the final reaction mixture consisting of a clear, red solution. Solvent was evaporated from this solution in vacuo, and the remaining residue was crystallized from hexanes (10 mL) at −15 °C to obtain 0.082 g (80% yield) of $CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}S_2CH_2SiMe_3)$ (**7**) as red crystals, mp 83 °C dec.

Complex **7** can also be obtained in similar yield by treating **6a** with an equimolar amount of sulfur in THF at 20 °C for 12 h.

**Preparation of $CpW(NO)(SCH_2SiMe_3)_2$ (8a).** A red solution of complex **7** (0.1 g, 0.2 mmol) in toluene (20 mL) was stirred vigorously at 35 °C for 20 h with no change in color. The final solution was taken to dryness in vacuo, and the remaining residue was extracted with hexanes (10 mL). Partial evaporation of the extracts and subsequent cooling to −15 °C induced the formation of red crystals. The crystals were collected by filtration to obtain 0.05 g (50% yield) of analytically pure $CpW(NO)(SCH_2SiMe_3)_2$ (**8a**), mp 91 °C dec.

**Table III. NMR Data for Complexes 3–8 in $C_6D_6$**

| | $^1$H NMR δ (*J*, Hz) | | | | | | | | $^{13}$C{$^1$H} NMR δ (*J*, Hz) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CH_2Si(CH_3)_3$ | | | W–$CH_2Si(CH_3)_3$ | | | | | $CH_2Si(CH_3)_3$ | | W–$CH_2Si(CH_3)_3$ | | $Y(CH_3)_3$ | | |
| | $C_5H_5$ | $CH_A$ | $H_B$ | $CH_3$ | $CH_A$ | $H_B$ | $CH_3$ | $Y(CH_3)_3$ | $C_5H_5$ | $CH_2$ | $CH_3$ | $CH_2$ | $CH_3$ | C | $CH_3$ | CN$^t$Bu |
| **3** | 5.02 (d)<br>($^3J_{^1H-^{31}P}$ = 2.5 Hz) | 0.08 (m) | | 0.55 | −0.43 (m) | | 0.24 | 0.95 (d)<br>($^2J_{^1H-^{31}P}$ = 9.1) | 97.90 | 7.25 (d)<br>($^2J_{^{13}C-^{31}P}$ = 14.0) | 4.39 | 6.07 (d)<br>($^2J_{^{13}C-^{31}P}$ = 9.3) | 4.21 | 12.66<br>($^1J_{^{13}C-^{31}P}$ = 29.3) | | |
| **4a** | 5.23 (s) | 3.10 (d)<br>($J_H{}^a$ = 11.2) | 2.39 (d) | 0.42 (s) | 1.03 (d)<br>($J_H$ = 12.7) | 0.40 (d) | 0.20 (s) | 1.14 (s) | 99.19 | 29.69 | 3.53 | −8.12<br>($J_W{}^b$ = 79.9) | −0.86 | 59.97 | 29.61 | 202.07 |
| **4b** | 5.17 (s) | | | 2.17 (s)<br>($CH_3$) | 1.11 (d)<br>($J_H$ = 12.7) | 0.39 (d) | 0.49 (s) | 1.00 (s) | 98.85 | | 20.84<br>($CH_3$) | −7.18<br>($J_W$ = 79.7) | 3.40 | 59.97 | 29.03 | 206.32 |
| **5**$^c$ | | | | | | | | | | | | | | | | |
| A | 5.43 (s) | 3.57 (d)<br>($J_H$ = 14.8) | 3.35 (d) | 0.35 (s) | 0.99 (d)<br>($J_H$ = 12.5) | 0.50 (d) | −0.03 (s) | | 103.79 | 47.51 | 3.55 | 15.24<br>($J_W$ = 75.3) | −2.61 | | | |
| B | 5.38 (s) | 3.54 (d)<br>($J_H$ = 14.6) | 3.34 (d) | 0.42 (s) | 1.42 (d)<br>($J_H$ = 12.2) | 1.03 (d) | 0.02 (s) | | 103.58 | 47.63 | 3.55 | 18.52<br>($J_W$ = 75.3) | −2.61 | | | |
| **6a** | 5.26 (s) | 4.12 (d)<br>($J_H$ = 13.6) | 3.59 (d) | 0.31 (s) | 1.05 (d)<br>($J_H$ = 11.4) | 0.77 (d) | 0.15 (s) | | 101.38 | 32.84 | 2.52 | 32.71<br>($J_W$ = 79.0) | −1.98 | | | |
| **6b** | 5.12 (s) | 4.20 (d)<br>($J_H$ = 13.2) | 3.61 (d) | 0.27 (s) | 0.86 (d)<br>($J_H$ = 10.8) | 0.61 (d) | 0.13 (s) | | 100.32 | 20.33 | 2.24 | 37.57<br>($J_W$ = 90.6) | −1.77 | | | |
| **7** | 5.12 (s) | 2.14 (d)<br>($J_H$ = 13.3) | 1.95 (d) | 0.47 (s) | 0.86 (d)<br>($J_H$ = 12.9) | 0.37 (d) | 0.09 (s) | | 100.97 | 31.71 | 3.76 | −3.22<br>($J_W$ = 78) | −1.64 | | | |
| **8a** | 5.29 (s) | 3.30 (d)<br>($J_H$ =14.0) | 3.16 (d) | 0.20 (s) | | | | | 101.55 | 30.35 | −1.76 | | | | | |
| **8b** | 5.14 (s) | 3.25 (d)<br>($J_H$ = 7.1) | 3.09 (d) | 0.16 (s) | | | | | 100.00 | 18.40 | −1.50 | | | | | |

$^a$ $J_H = {}^2J_{^1H_A-^1H_B}$. $^b$ $J_W = {}^1J_{^{13}C-^{183}W}$. $^c$ A:B ratio = 4:1.

**Table IV. Crystallographic Data for $(\eta^5\text{-}C_5H_5)W(NO)(CH_2SiMe_3)_2$ (2a)$^a$**

| | |
|---|---|
| formula | $C_{13}H_{27}NOSi_2W$ |
| fw | 453.38 |
| cryst system | monoclinic |
| space group | $P2_1/c$ |
| *a* (Å) | 12.070 (2) |
| *b* (Å) | 12.4360 (7) |
| *c* (Å) | 13.5742 (15) |
| α (deg) | 90 |
| β (deg) | 104.856 (6) |
| γ (deg) | 90 |
| *V* (Å$^3$) | 1969.4 (4) |
| *Z* | 4 |
| $D_{calcd}$ (g/cm$^3$) | 1.529 |
| *F*(000) | 888 |
| ±(Mo Kα) (cm$^{-1}$) | 61.0 |
| cryst dimens (mm) | 0.29 × 0.34 × 0.52 |
| transmissn factors | 0.098–0.230 |
| scan type | ω/2θ |
| scan range (deg in ω) | 0.75 + 0.35 tan θ |
| scan speed (deg/min) | 1.01–10.06 |
| data collected | ±*h*,+*k*,+*l* |
| $2\theta_{max}$ (deg) | 60 |
| unique reflctns | 5715 |
| reflectns with $I \geq 3\sigma(I)$ | 2654 |
| no. of variables | 163 |
| *R* | 0.048 |
| $R_w$ | 0.050 |
| *S* | 2.135 |
| mean Δ/σ (final cycle) | 0.02 |
| max Δ/σ (final cycle) | 0.24 |
| residual density (e/Å$^3$) | −3.3 to +1.5 (near W) |

$^a$ Temperature 22 °C. Enraf-Nonius CAD4-F diffractometer, Mo Kα radiation ($\lambda_{K\alpha_1}$ = 0.709 30, $\lambda_{K\alpha_2}$ = 0.713 59 Å), graphite monochromator, takeoff angle 2.7°, aperture (2.00 + tan θ) × 4.0 mm at a distance of 173 mm from the crystal, scan range extended by 25% on both sides for background measurement, $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$ (*S* = scan count, *B* = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$. Values given for *R*, $R_w$, and *S* are based on those reflections with $I \geq 3\sigma(I)$.

The isomerization of **7** to **8a** was effected several times in $C_6D_6$ at 35 °C, and its progress was monitored by $^1$H NMR spectroscopy. This monitoring indicated that even though **8a** was initially formed cleanly, it soon began to convert slowly to another species. Regrettably, numerous attempts to isolate and identify this species have not been successful. The procedure for obtaining **8a** outlined in the preceding paragraph thus represents the optimum balance involving the maximum conversion of **7** to **8a** and the minimum decomposition of **8a**.

Complex **8a** can also be obtained directly in 50–55% yields by treating **2a** or **6a** with a slight excess (2–3 equiv) of elemental sulfur in toluene or hexanes at 75–85 °C for 24–36 h.

**Preparation of CpW(NO)(SeCH$_2$SiMe$_3$)$_2$ (8b).** A violet solution of **2a** (0.45 g, 1.0 mmol) in THF (40 mL) was treated with an excess (0.40 g, 0.50 mmol) of gray selenium, and the heterogeneous mixture thus formed was stirred rapidly at 40–50 °C. After 18 h, the supernatant solution had become red in color, and the amount of undissolved selenium had diminished. The final mixture was taken to dryness in vacuo, and the remaining residue was extracted with hexanes (35 mL). Slow concentration of the extracts under reduced pressure at 0 °C induced the formation of orange-red crystals. These crystals were collected by filtration and dried at 5 × 10$^{-3}$ Torr and 20 °C to obtain 0.33 g (55% yield) of CpW(NO)(SeCH$_2$SiMe$_3$)$_2$ (**8b**).

Complex **8b** can also be obtained in similar yields by treating **2a** with 2 equiv of red selenium in THF or toluene at room temperature for 36 h.

**X-ray Crystallographic Analysis of CpW(NO)(CH$_2$SiMe$_3$)$_2$.** Crystallographic data appear in Table IV. Final unit-cell parameters were obtained by least-squares analysis of 2(sin θ)/λ values for 25 reflections with 2θ = 30–35°. The intensities of three standard reflections, measured each hour of X-ray exposure time during the data collection, decayed uniformly

**Table V. Final Positional (Fractional × $10^4$, W and Si × $10^5$) and Isotropic Thermal Parameters ($U \times 10^3$ Å$^2$) for the Non-Hydrogen Atoms of $CpW(NO)(CH_2SiMe_3)_2$ (2a)**

| atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| W | 42932 (3) | 31562 (2) | 31704 (3) | 64 |
| Si(1) | 15611 (24) | 19999 (25) | 28652 (27) | 94 |
| Si(2) | 71769 (25) | 26729 (29) | 44541 (24) | 91 |
| O | 4129 (8) | 3263 (5) | 5314 (5) | 107 |
| N | 4221 (7) | 3116 (5) | 4446 (6) | 77 |
| C(1) | 2986 (8) | 2036 (7) | 2580 (9) | 84 |
| C(2) | 5903 (8) | 2395 (7) | 3430 (7) | 76 |
| C(3) | 3486 (12) | 4842 (8) | 2754 (9) | 103 |
| C(4) | 3235 (11) | 4263 (8) | 1820 (8) | 99 |
| C(5) | 4269 (13) | 4056 (9) | 1562 (8) | 104 |
| C(6) | 5138 (10) | 4513 (8) | 2341 (9) | 104 |
| C(7) | 4717 (14) | 4961 (9) | 3055 (8) | 112 |
| C(8) | 1752 (15) | 1536 (22) | 4169 (16) | 281 |
| C(9) | 782 (18) | 3257 (17) | 2582 (33) | 274 |
| C(10) | 604 (17) | 1048 (33) | 2043 (22) | 332 |
| C(11) | 6908 (12) | 2218 (19) | 5725 (12) | 177 |
| C(12) | 7526 (17) | 4131 (15) | 4565 (16) | 213 |
| C(13) | 8426 (11) | 1872 (12) | 4253 (14) | 146 |

**Table VI. Bond Lengths (Å) for $CpW(NO)(CH_2SiMe_3)_2$**

| | | | |
|---|---|---|---|
| W–N | 1.757 (8) | Si(1)–C(10) | 1.82 (2) |
| W–C(1) | 2.103 (9) | Si(2)–C(2) | 1.822 (10) |
| W–C(2) | 2.108 (9) | Si(2)–C(11) | 1.92 (2) |
| W–C(3) | 2.319 (10) | Si(2)–C(12) | 1.86 (2) |
| W–C(4) | 2.385 (10) | Si(2)–C(13) | 1.884 (13) |
| W–C(5) | 2.447 (10) | O–N | 1.226 (10) |
| W–C(6) | 2.397 (10) | C(3)–C(4) | 1.422 (14) |
| W–C(7) | 2.316 (11) | C(3)–C(7) | 1.44 (2) |
| Si(1)–C(1) | 1.858 (11) | C(4)–C(5) | 1.40 (2) |
| Si(1)–C(8) | 1.79 (2) | C(5)–C(6) | 1.405 (14) |
| Si(1)–C(9) | 1.81 (2) | C(6)–C(7) | 1.33 (2) |

**Table VII. Bond Angles (deg) for $CpW(NO)(CH_2SiMe_3)_2$**

| | | | |
|---|---|---|---|
| N–W–C(1) | 97.7 (4) | C(11)–Si(2)–C(12) | 107.5 (10) |
| N–W–C(2) | 95.7 (4) | C(11)–Si(2)–C(13) | 107.5 (8) |
| C(1)–W–C(2) | 109.6 (4) | C(12)–Si(2)–C(13) | 110.7 (10) |
| C(1)–Si(1)–C(8) | 108.4 (7) | W–N–O | 169.5 (6) |
| C(1)–Si(1)–C(9) | 113.1 (8) | W–C(1)–Si(1) | 125.5 (5) |
| C(1)–Si(1)–C(10) | 111.3 (9) | W–C(2)–Si(2) | 127.1 (5) |
| C(8)–Si(1)–C(9) | 114 (2) | C(4)–C(3)–C(7) | 105.8 (11) |
| C(8)–Si(1)–C(10) | 106.8 (13) | C(3)–C(4)–C(5) | 108.4 (11) |
| C(9)–Si(1)–C(10) | 102.5 (15) | C(4)–C(5)–C(6) | 106.1 (11) |
| C(2)–Si(2)–C(11) | 109.0 (6) | C(5)–C(6)–C(7) | 111.6 (12) |
| C(2)–Si(2)–C(12) | 112.1 (6) | C(3)–C(7)–C(6) | 108.1 (10) |
| C(2)–Si(2)–C(13) | 109.9 (6) | | |

to final values about 6% less than their initial values. The data were scaled accordingly and corrected for absorption by using the Gaussian integration method;[23-25] the range of transmission factors is given in Table IV.

The structure was solved by conventional heavy-atom methods, the coordinates of the W and Si atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from a subsequent difference map. During the final stages of full-matrix least-squares refinement, the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included as fixed contributors in idealized positions (methyl groups staggered in accordance with observed hydrogen positions, C(sp$^2$)–H = 0.97 Å, C(sp$^3$)–H = 0.98 Å, $U_H \propto U_{parent}$), recalculated after each cycle of refinement. Neutral atom scattering factors for all atoms and anomalous scattering corrections for W and Si were taken from ref 26.

Final positional and equivalent isotropic thermal parameters ($U_{eq} = {}^1/_3 \times$ trace diagonalized $U$) are given in Table V. Bond lengths and angles appear in Tables VI and VII, respectively. Calculated hydrogen parameters, anisotropic thermal parameters, torsion angles, and structure factor amplitudes (Tables VIII–XI) are provided as supplementary material.

## Results and Discussion

**Syntheses and Physical Properties of the Complexes $[CpM(NO)(CH_2SiMe_3)_2]_2MgI_2{\cdot}Et_2O$ (1; M = Mo or W) and $CpM(NO)R_2$ (2; M = Mo, R = $CH_2SiMe_3$; M = W, R = $CH_2SiMe_3$, $CH_2CMe_3$, $CH_2CMe_2Ph$, or $CH_2Ph$).** These alkyl complexes can be conveniently prepared by the sequential transformations shown in eq 4 and 5. The desired nitrosyl-containing products of both

$$[CpM(NO)I_2]_2 + 4RMgCl \xrightarrow[0\,°C]{Et_2O} [CpM(NO)R_2]_2MgI_2{\cdot}Et_2O + 3MgX_2(Et_2O)_n \quad (4)$$
$$X = Cl \text{ or } I$$

$$[CpM(NO)R_2]_2MgI_2{\cdot}Et_2O + 6H_2O \xrightarrow[20\,°C]{Et_2O} 2CpM(NO)R_2 + [Mg(H_2O)_6]^{2+} + 2I^- + Et_2O \quad (5)$$

reactions are isolable in good yields as crystals from the final reaction mixtures by fractional crystallization if M = Mo or W and R = $CH_2SiMe_3$. On the other hand, when M = W and R = $CH_2CMe_3$, $CH_2CMe_2Ph$, or $CH_2Ph$, reaction 4 produces yellow precipitates. Nevertheless, treatment of these precipitates in $Et_2O$ with $H_2O$ (as in eq 5) does afford the respective $CpW(NO)R_2$ complexes in isolated yields of 35–55%. The presence of monoalkylated complexes has not been detected in any case. Indeed, if less than 4 equiv of the Grignard reagent are employed in reaction 4, lower yields of the $CpM(NO)R_2$ complexes are eventually obtained from reaction 5 along with some unreacted $[CpM(NO)I_2]_2$ dimers. Furthermore, attempts to utilize reactions 4 and 5 to prepare $CpM(NO)R_2$ complexes having small alkyl groups (e.g. R = Me), alkyl groups having β-hydrogens (e.g. R = Et), or aryl groups (e.g. R = Ph) have so far been unsuccessful. It thus appears that the $CpM(NO)R_2$ complexes that have been isolated during this work owe their stability to the fact that they are relatively kinetically inert by virtue of not having an energetically accessible decomposition pathway. Nevertheless, the fact that the compounds having the sterically demanding R groups have been obtained suggests that the other $CpM(NO)R_2$ species mentioned above may well be accessible by other synthetic routes.[27] Alternatively, they may be stabilized by complexation with appropriate Lewis bases after being prepared (vide infra).

The intermediate alkyl complexes $[CpM(NO)(CH_2SiMe_3)_2]_2MgI_2{\cdot}Et_2O$ (M = W, **1a**; M = Mo, **1b**) isolated from reaction 4 are red, diamagnetic crystalline solids. They are most soluble in solvents such as $Et_2O$ and THF,[28] and they are air-sensitive both in solution and in the solid state. As solids, **1a** and **1b** are thermally stable at 20 °C under $N_2$ for at least 3 months, but their solutions under identical conditions deposit insoluble yellow-red precipitates in a matter of days. Interestingly enough, treatment of these precipitates with $H_2O$ does afford the corresponding $CpM(NO)(CH_2SiMe_3)_2$ (M = W, **2a**; M = Mo, **2b**) compounds, albeit in lower yields than if the $H_2O$ is added soon after the formation of **1a** and **1b** via reaction

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(23) The computer programs used include locally written programs for data processing and locally modified versions of the following: ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin and H. A. Levy; FORDAP, Patterson and Fourier syntheses, by A. Zalkin; ORTEP II, illustrations, by C. K. Johnson.

(24) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.

(25) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1967**, *22*, 457.

(26) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(27) The existence of $Cp^*Mo(NO)Me_2$ has been claimed; see, Alcañiz, E. de J. Ph.D. Dissertation, Universidad de Alcalá de Henares, Madrid, Spain, 1987.

(28) Drago, R. S. *Pure Appl. Chem.* **1980**, *52*, 2261.

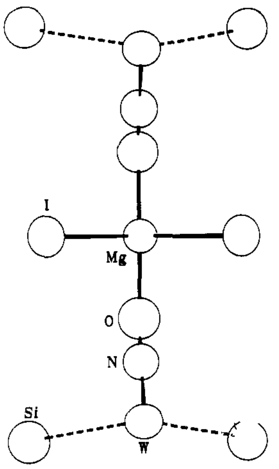

**Figure 1.** Partial solid-state molecular structure of **1a** exhibiting $C_{2v}$ symmetry. Selected interatomic distances (Å) and angles (deg): W–N = 1.77, Mg–I = 2.76, Mg–O = 2.11, N–O = 1.20, Si···W = 3.47; I–Mg–I′ = 112.0, I–Mg–O = 95.7, O–Mg–O′ = 159.2, W–N–O = 169.0, Mg–O–N = 135.6.

4. The formulations of both **1a** and **1b** are based on their spectroscopic properties (Tables I and II) and on partial X-ray crystallographic analyses of single crystals of each.[22] The complexes are isostructural and possess crystallographic *mm*2 ($C_{2v}$) symmetry in the solid state, as illustrated for **1a** in Figure 1. They involve two CpM(NO)($CH_2SiMe_3$)$_2$ molecules functioning as Lewis bases via the oxygen atoms of their nitrosyl ligands toward the Lewis acid sites on the Mg atoms. The existence of this isonitrosyl[29] linkage is also indicated by the IR spectra of **1a** and **1b** as Nujol mulls which exhibit $\nu_{NO}$'s at 1505 and 1520 cm$^{-1}$, respectively. These absorptions are 36 and 67 cm$^{-1}$, respectively, lower in energy than the nitrosyl-stretching frequencies exhibited by the uncomplexed CpM(NO)($CH_2SiMe_3$)$_2$ molecules (**2a** and **2b**) in the solid state. The NO→Mg←ON interactions persist when **1a** and **1b** are dissolved in noncoordinating solvents such as benzene[28] (Table I), but they are cleaved upon exposure to molecules that are stronger Lewis bases than **2a** or **2b**. Hence, treatment of **1a** or **1b** with an excess of $H_2O$ results in the occurrence of reaction 5 and the liberation of **2a** or **2b**.

Complexes **2a** and **2b** and the other similarly obtainable CpW(NO)$R_2$ dialkyl complexes (i.e. R = $CH_2CMe_3$, **2c**; R = $CH_2CMe_2Ph$, **2d**; R = $CH_2Ph$, **2e**) are violet to red, diamagnetic solids that are soluble in all common organic solvents. In solutions and in the solid state the compounds (excepting **2a**) are quite air-sensitive and must be maintained in an inert atmosphere. Their spectroscopic properties (summarized in Tables I and II) are consistent with their possessing three-legged piano-stool molecular structures. Particularly notable are the very low $\nu_{NO}$'s (1597–1625 cm$^{-1}$) evident in their IR spectra in hexanes which are reflective of the existence of considerable M→NO back-bonding in these compounds even though they are formally 16-electron species. [For comparison, the related 18-electron complex Cp*Ru(NO)$Et_2$ exhibits a $\nu_{NO}$ at 1720 cm$^{-1}$ in $C_6H_6$.[8a]]

A single-crystal X-ray crystallographic analysis of **2a** (Table IV) has confirmed its monomeric nature[30] and its molecular structure having a noncrystallographic mirror plane (Figure 2). The intramolecular geometrical parameters of the molecule are presented in Tables VI and VII. The most chemically interesting feature of the structure involves the essentially linear (169.5 (6)°) WNO group in which the short W–N (1.757 (8) Å) and long N–O (1.226 (10) Å) bond lengths substantiate the inference of considerable W→NO back-bonding[32] from the IR data (vide supra). The Cp–W and W–$CH_2SiMe_3$ intramolecular dimensions are comparable to those found in related complexes.[33,34] In particular, the methylene hydrogens of the $CH_2SiMe_3$ ligands are found in normal tetrahedral positions. Hence, there is no evidence for any C–H⇀W agostic[35] interactions involving the methylene fragments in the solid state. In general, the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of complexes **2** (Table II) confirm that their molecular structures in solution are analogous to that presented for **2a** in Figure 2. Hence, the presence of diasterotopic methylene protons is clearly evident in all the $^1H$ NMR spectra. Nevertheless some of the signals due to these protons occur at relatively high fields, thereby suggesting[35] the possibility of some C–H⇀W interactions. The most upfield chemical shifts of the signals due to the $CH_2$ protons occur in the $^1H$ NMR spectrum of complex **2c** (Table II). Consistently, the $^{13}C$-gated decoupled NMR spectrum of this compound in $C_6D_6$ exhibits $J_{^{13}C-^1H_A}$ = 100.1 Hz, a relatively low value indicative of the electron-deficient metal center interacting somewhat with the methylene C–H bond of the alkyl ligand.[35] Hence, it is probable that similar interactions occur to some extent for all the complexes **2** in solutions. These C–H⇀M links, if they do exist, do not apparently affect the characteristic chemistry of these compounds.

**Some Chemical Properties of CpW(NO)($CH_2SiMe_3$)$_2$ (2a).** Of the four complexes **2** prepared during this work, the one isolable in the highest yield is **2a**. In addition, the reactivity of this complex with various substrates may be conveniently monitored by conventional spectroscopic techniques. For these reasons, **2a** was chosen as the prototypal CpM(NO)$R_2$ complex with which to investigate some of the chemical properties of these systems.

Under $N_2$ at ambient temperatures, violet crystals of **2a** are reasonably thermally and photolytically stable for days. However, storage of the crystals (either under $N_2$ or under vacuum) for 1 month at 20 °C causes their decomposition to the oxo alkylidene complex CpW(O)($CHSiMe_3$)($CH_2SiMe_3$),[33a] as the only identifiable product in 40–45% yield. No nitrosyl-containing decomposition products can be detected by IR spectroscopy. Consequently, for storage over longer periods of time, **2a** is best kept as a solid under $N_2$ at 0 °C in the dark.

As noted in the preceding section, **2a** is soluble in common organic solvents, and the resulting violet solutions are quite thermally and photolytically stable. For instance, thermolysis at 70 °C or photolysis at 20 °C of **2a** in benzene solution (in the presence or absence of $PMe_3$) for 1–2 days leads to decomposition of only 10% of the starting material to an intractable red-brown solid. Evidently, the steric bulk of the ligands attached to the tungsten center in **2a** impedes the traversal of possible decomposition pathways.

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[29] Crease, A. E.; Legzdins, P. *J. Chem. Soc., Dalton Trans.* **1973**, 1501 and references therein.

[30] In the solid state, weakly associated centrosymmetric dimers are formed via methyl C–H···O hydrogen bonding[31] about the inversion center at ($^1/_2$, $^1/_2$, $^1/_2$) [C(7)–H(7)···(1 – *x*, 1 – *y*, 1 – *z*), H···O = 2.27 Å, C···O = 3.18 (1) Å, C–H···O = 155°, N–O···H = 126°]. This hydrogen bonding results in the lowest $\nu_{NO}$ of **2a** being in the solid state (see Table I).

[31] Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

[32] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. L. *Inorg. Chem.* **1979**, *18*, 116 and references therein.

[33] (a) Legzdins, P.; Rettig, S. J.; Sánchez, L. *Organometallics* **1985**, *4*, 1470. (b) Evans, S. V.; Legzdins, P.; Rettig, S. J.; Sánchez, L.; Trotter, J. *Ibid.* **1987**, *6*, 7.

[34] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Stults, B. R. *Inorg. Chem.* **1976**, *15*, 2252.

[35] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

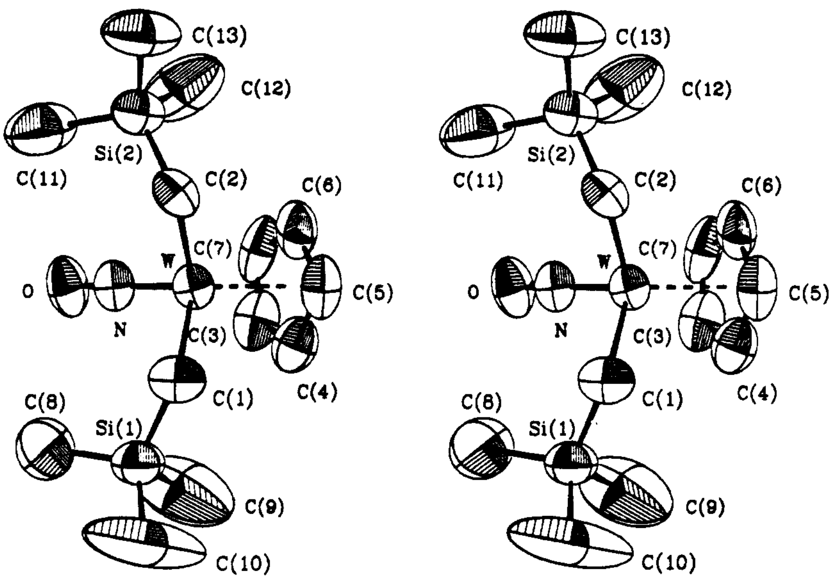


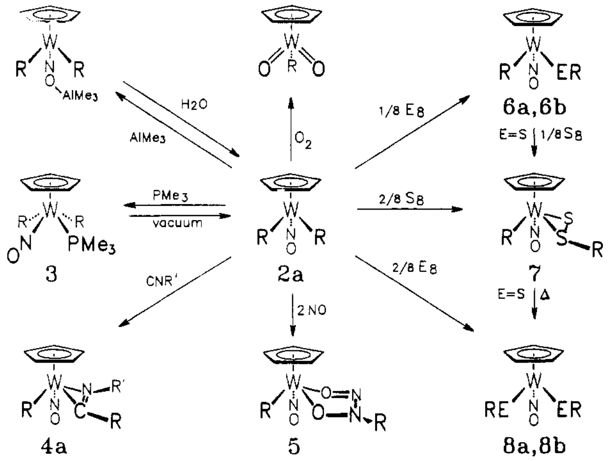
**Figure 2.** Stereoview of the molecular structure of **2a**. Hydrogen atoms have been omitted for clarity.

Furthermore, the valence electronic structure of **2a** (reflecting the strong $\pi$-acidity of the NO ligand) is also consistent with it exhibiting reasonable thermal stability.[13a]

Either as a solid or in solution, **2a** reacts with $O_2$ to afford principally the white dioxo alkyl complex $CpW(O)_2(CH_2SiMe_3)$[33a] in high yields. As a result, the reactions of **2a** with the various reactants outlined below must be effected under rigorously $O_2$-free conditions in order to avoid the contamination of the desired products by some $CpW(O)_2(CH_2SiMe_3)$. On the other hand, solutions of **2a** are much less sensitive to $H_2O$, as evidenced by the occurrence of reaction 5. Thus, $Et_2O$ or THF solutions of **2a** at 20 °C undergo no change in 1 or 2 days when treated with an excess of $O_2$-free water. After 1 week, however, these mixtures do begin to deposit slowly a white, insoluble precipitate whose IR spectrum as a Nujol mull is devoid of absorptions attributable to Cp, $CH_2SiMe_3$, and NO ligands.

The reactivity with $O_2$ and the rest of the chemistry of **2a** that has been discovered during the present study is summarized in Scheme I.

**Scheme I**



R=CH2SiMe3, R' =t-Bu, E=S,Se

**Reactions with Lewis Acids.** The Lewis basicity of the oxygen atom of the nitrosyl ligand in **2a** has been manifested by the existence of isonitrosyl linkages in **1a**. Hence, it is not surprising that hard Lewis acids such as $AlMe_3$ form red 1:1 adducts with **2a** via its NO group,[36] as depicted in Scheme I. These adducts as Nujol mulls exhibit a $\nu_{NO}$ of ~1500 cm$^{-1}$ which is very similar to that displayed by **1a** under identical conditions (Table I). As with **1a** (cf. eq 5), treatment of **2a**·$AlMe_3$ with $H_2O$ regenerates the starting dialkyl complex.

**Reactions with Lewis Bases. (a) $PMe_3$.** The results of Fenske–Hall MO calculations on the model compound $CpMo(NO)Me_2$ have been used to rationalize the thermal stability and the low $\nu_{NO}$'s exhibited by the 16-electron $CpM(NO)R_2$ complexes.[13a] These calculations also indicate that the LUMO of these molecules is a nonbonding, metal-localized orbital that should confer Lewis acid properties on these electron-deficient compounds. Superimposed on these expectations in the case of **2a** is the fact that the accessibility of its LUMO to incoming bases will also be restricted somewhat by the sheer steric bulk of its hydrocarbon ligands.[37] Indeed, during the course of this research, we have found that **2a** is most prone to react with small, strongly basic molecules. Hence, it readily forms a 1:1 adduct in hexanes solution with $PMe_3$ (Scheme I) but does not incorporate the more sterically demanding $PMePh_2$ or $PPh_3$.[39] Furthermore, its solutions are unaffected by treatment with 2–3 atm of the relatively weak Lewis bases $N_2$, $C_2H_4$, or $CO_2$.

The monophosphine adduct $CpW(NO)(CH_2SiMe_3)_2(PMe_3)$ (**3**) is an air-sensitive, lemon yellow solid which loses $PMe_3$ and reverts back to **2a** when exposed to 5 × $10^{-3}$ Torr at 20 °C for 2 days (Scheme I). It is only slightly soluble in hexanes but is quite soluble in more polar solvents to produce air-sensitive, yellow solutions. The IR spectrum of **3** as a Nujol mull displays strong absorptions at 950 and 1520 cm$^{-1}$ attributable to the $PMe_3$ and the NO ligands, respectively. The latter absorption is 21 cm$^{-1}$ lower in energy than that exhibited by the parent **2a** and is

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(36) Subsequent work has shown that these adducts are isolable as analytically pure solids: Brunet, N.; Legzdins, P., unpublished observations.

(37) It has been demonstrated for other coordinatively unsaturated, 16-electron molecules such as $M(CO)_3(PR_3)_2$ (M = Mo, W; R = bulky alkyl) and $Mo(diphos)_2(CO)$ that their ability to bind additional ligands is strongly influenced by steric factors.[38]

(38) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294 and references therein.

(39) For a discussion of the Lewis basicities and steric requirements of phosphines see: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 31.

reflective of increased electron density at the metal center in **3** and concomitantly greater W→NO back-bonding. The $^{31}P\{^1H\}$ NMR spectrum of **3** in $C_6D_6$ consists of a single signal at $\delta$ −15.0 whose $^{183}W$ satellites confirm that the phosphine is directly attached to the tungsten atom. Finally, the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **3** in $C_6D_6$ (Table III) display two sets of signals due to the alkyl ligands, thereby indicating that these ligands are in magnetically different environments. For instance, the $^{13}C\{^1H\}$ NMR spectrum exhibits two doublets at $\delta$ 7.25 and 6.07 with $^2J_{^{13}C-^{31}P}$ of 14.0 and 9.3 Hz, respectively, which may be assigned to the methylene carbons of the two $CH_2SiMe_3$ ligands. These physical properties are most consistent with **3** possessing a monomeric four-legged piano-stool molecular structure in which the two alkyl groups are cis, as depicted in Scheme I.

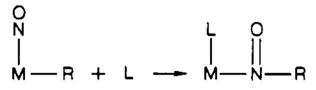
The formation of the adduct **3** by the treatment of **2a** with $PMe_3$ is essentially quantitative. There is no evidence for the accompanying occurrence of the intramolecular insertion of the bound nitrosyl ligand into one of the $W-CH_2SiMe_3$ linkages, i.e. eq 6, as has been observed to

$$CpW(NO)(CH_2SiMe_3)_2 + PMe_3 \not\rightarrow CpW[N(=O)CH_2SiMe_3](CH_2SiMe_3)(PMe_3) \quad (6)$$

occur for some other alkyl nitrosyl complexes.[9] Furthermore, **3** itself also does not undergo such intramolecular transformations, i.e. eq 7. In other words, neither the 16-

$$CpW(NO)(CH_2SiMe_3)_2(PMe_3) + PMe_3 \not\rightarrow CpW[N(=O)CH_2SiMe_3](CH_2SiMe_3)(PMe_3)_2 \quad (7)$$

nor the 18-electron nitrosyl alkyl complexes of tungsten isolated during this study are prone to effect spontaneously the migratory insertion of NO. Indeed, as described in detail below, the 16-electron **2a** only inserts external nucleophiles into its W–C bonds. Hence, judging by the rate of the reaction



$$\overset{\overset{O}{N}}{\underset{|}{M}}—R + L \rightarrow \overset{L}{\underset{|}{M}}—\overset{O}{\underset{\|}{N}}—R \quad (8)$$

under ambient conditions, the tendency for alkyl nitrosyl complexes to undergo insertion 8 decreases in the order M = CpCo > CpFeR >>> CpWR, a trend for which there is no ready explanation at present. Nevertheless, the insertions 8 that do occur have been empirically optimized for the purpose of synthesizing new carbon–nitrogen bonds.[9]

**(b) CO and *t*-BuNC.** Bubbling CO through a purple hexanes solution of **2a** at −20 °C rapidly (1 min or less) produces a yellow precipitate which exhibits $\nu_{NO}$'s at 1635 and 1575 $cm^{-1}$ in its IR spectrum as a Nujol mull under ambient conditions. Under these conditions, however, the precipitate decomposes quickly both in the solid state and in solutions ($Et_2O$ or $C_6H_6$) to an intractable brown powder. On the other hand, solutions of the yellow precipitate are thermally stable at −78 °C and quantitatively afford complex **3** when $PMe_3$ is added. It thus appears that CO initially coordinates to the metal center to form the $CpW(NO)(CH_2SiMe_3)_2(CO)$ adduct analogous to **3**. Not surprisingly, the CO ligand in this adduct is easily displaced by the more basic[39] $PMe_3$ at low temperatures. Upon warming to −20 °C or higher temperatures, however, the CO adduct undergoes further transformations to the intractable brown powder.

In contrast, the reaction of **2a** with *t*-BuNC (a formal bulky analogue of CO) is quite straightforward, i.e. eq 9. Transformation 9 occurs under very mild conditions, and the insertion product **4a** is isolable in 94% yield as a pale yellow, crystalline solid by crystallization of the dried final

$$\underset{\mathbf{2a}}{CpW(NO)(CH_2SiMe_3)_2} + t\text{-BuNC} \xrightarrow[-78\ °C]{THF} \underset{\mathbf{4a}}{CpW(NO)(CH_2SiMe_3)[\eta^2\text{-}C(CH_2SiMe_3)=N\text{-}t\text{-Bu}]} \quad (9)$$

reaction mixture from $Et_2O$ at −20 °C. Complex **4a** is an air- and water-sensitive species that has been fully characterized by elemental analyses and conventional spectroscopic methods (Tables I and III). All the physical data are consistent with the iminoacyl ligand of **4a** being attached to the metal center in a $\eta^2$ fashion as shown in Scheme I. Thus, the $\nu_{CN}$ of 1685 $cm^{-1}$ exhibited by **4a** in its IR spectrum as a Nujol mull (Table I) is in the range of $\nu_{CN}$'s found for other $\eta^2$-iminoacyl groups bound to group 6 metal centers.[40] Also, the resonance due to the alkyl $\alpha$-carbon of the iminoacyl ligand at 202.07 ppm evident in the $^{13}C\{^1H\}$ NMR spectrum of **4a** in $C_6D_6$ (Table III) compares well with the chemical shift values previously reported for the $\alpha$-carbons of other $\eta^2$-iminoacyl complexes.[40] It seems likely that reaction 9 proceeds in a stepwise fashion, the first step involving the coordination of the *t*-BuNC molecule to the tungsten center of **2a** to form an adduct analogous to **3**. The second step would be a very rapid intramolecular migratory insertion reaction of the *t*-BuNC ligand into one of the W–alkyl linkages of the adduct. These two steps would afford the final complex **4a** in which the metal center attains the favored 18-valence-electron configuration by virtue of the $\eta^2$-iminoacyl ligand functioning as a formal three-electron donor.

As with other $\eta^2$-acyl[41] and -iminoacyl[42] complexes containing (trimethylsilyl)methyl groups in their $\eta^2$-ligands, the hydrolytic cleavage of the $Me_3Si-CH_2$ bond of the iminoacyl group in **4a** can be easily effected under mild conditions, i.e. eq 10, the corresponding methyl derivative

$$\underset{\mathbf{4a}}{CpW(NO)(CH_2SiMe_3)[\eta^2\text{-}C(CH_2SiMe_3)=N\text{-}t\text{-Bu}]} + H_2O \xrightarrow[20\ °C]{THF} \underset{\mathbf{4b}}{CpW(NO)(CH_2SiMe_3)[\eta^2\text{-}C(CH_3)=N\text{-}t\text{-Bu}]} + Me_3SiOH \quad (10)$$

**4b** being the sole organometallic nitrosyl product. The spectroscopic properties of **4b** are quite similar to those exhibited by **4a** (Tables I and III). Hence, it is highly likely that it too contains an $\eta^2$-iminoacyl ligand and a tungsten center having an 18-electron configuration.

**(c) NO.** Reaction of **2a** in hexanes with NO gas proceeds rapidly to completion (~10 min at room temperature) to afford quantitatively product **5** (Scheme I) as a yellow, crystalline, air-stable solid, i.e. eq 11. Reaction

$$\underset{\mathbf{2a}}{Cp(W)(NO)(CH_2SiMe_3)_2} + 2NO \xrightarrow[20\ °C]{hexanes} \underset{\mathbf{5}}{CpW(NO)(CH_2SiMe_3)(\eta^2\text{-}O_2N_2\{CH_2SiMe_3\})} \quad (11)$$

11 involves the insertion of two molecules of NO into one W–C bond of **2a** to produce **5** which contains a chelating *N*-alkyl-*N*-nitrosohydroxylaminato ligand. By reacting with nitric oxide in this fashion, **2a** thus resembles other

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[40] Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L.; Latesky, S. L.; McMullen, A. K.; Rothwell, I. P.; Folting, K.; Huffman, J. C.; Streib, W. E.; Wang, R. *J. Am. Chem. Soc.* **1987**, *109*, 390 and references cited therein.

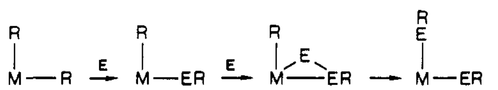
[41] (a) Carmona, E.; Sánchez, L.; Marín, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214. (b) Carmona, E.; Sánchez, L., unpublished observations.

[42] Palma, P. Ph.D. Dissertation, Universidad de Sevilla, Seville, Spain, 1986.

diamagnetic alkyls,[43] most notably the related 16-electron $Cp_2ZrR_2$ species.[44] Evidently, the inability of the tungsten center in **5** to increase its coordination number further once it has attained the 18-valence-electron configuration precludes the second alkyl ligand from becoming involved in the reaction with external NO.

The presence of the terminal nitrosyl ligand and the $\eta^2$-$O_2N_2(R)$ group in **5** are clearly indicated by the IR spectrum of the complex as a KBr pellet. Hence, this spectrum exhibits a strong absorption at 1588 $cm^{-1}$ characteristic of the former ligand and three medium intensity bands at 1235, 1190, and 935 $cm^{-1}$ diagnostic of the latter group.[43] Indeed, the elemental analysis and mass spectral and $^1H$ and $^{13}C\{^1H\}$ NMR spectral data for **5** (Tables I and III) are consistent with it possessing a four-legged piano-stool molecular structure as depicted in Scheme I. In fact, just this structure has been established for **5** in the solid state by a single-crystal X-ray crystallographic analysis, the full details of which will be published elsewhere.[45] Interestingly, the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **5** also indicate that in nonpolar solvents the complex exists as a mixture of two isomers, designated A and B in Table III. In $C_6D_6$, for instance, the isomer ratio A:B $\simeq$ 4:1 at 20 °C, but in more polar solvents such as $CDCl_3$ only isomer B persists. The two isomers A and B probably differ only in the orientation of the R substituent of the planar $\eta^2$-$O_2N_2(R)$ group either away from or toward (as in Scheme I) the alkyl ligand. Exchange between isomers of this type presumably occurs either by rotation of the $\eta^2$-$O_2N_2(R)$ group or via an $\eta^2$–$\eta^1$–$\eta^2$ rearrangement involving essentially complete dissociation of one of the oxygen donor atoms from the tungsten. The existence of similar isomers for related complexes containing $\eta^2$-acyl and $\eta^2$-iminoacyl ligands has been previously documented.[40] Nevertheless, the two related $\eta^2$-iminoacyl complexes isolated during the present study (i.e. **4a** and **4b**) do not exhibit isomerism analogous to that displayed by complex **5**.

**(d) $S_8$ and $Se_8$.** As noted above, treatment of the parent dialkyl nitrosyl complex **2a** with elemental oxygen results in the production of $CpW(O)_2(CH_2SiMe_3)$. The analogous reactions of **2a** with elemental sulfur and selenium, however, do not result in the formation of $CpW(E)_2(CH_2SiMe_3)$ (E = S or Se) species. Rather, **2a** undergoes the sequential transformations summarized in eq 12 where M = CpW(NO) to afford $CpW(NO)(ECH_2SiMe_3)_2$ complexes (E = S (**8a**) or Se (**8b**)) as the final isolable products. When E = S in eq 12 both the intermediate compounds $CpW(NO)(CH_2SiMe_3)(SCH_2SiMe_3)$ (**6a**) and $CpW(NO)(CH_2SiMe_3)(\eta^2$-$S_2CH_2SiMe_3)$ (**7**) formed by the insertion of elemental sulfur into W–C $\sigma$-bonds are isolable. On the other hand, when E = Se, only the first intermediate complex $CpW(NO)(CH_2SiMe_3)(SeCH_2SiMe_3)$ (**6b**) can be isolated. The new complexes **6**–**8** may also be synthesized directly from **2a** (Scheme I) by employing the conditions specified in the Experimental Section.[46] They are all obtainable as crystalline, diamagnetic solids that are soluble in common organic solvents to give moderately air-sensitive solutions. They have been fully characterized by conventional methods, including single-crystal X-ray crystallographic analyses of **6a** and **7**.[33b] These latter analyses establish that both complexes are monomeric in the solid state and possess the customary piano-stool molecular structures. In **6a**, a short (2.301 (2) Å) W–S bond indicates significant multiple-bond character for this linkage in the formally 16-electron complex. In comparison, **7** is an 18-electron compound, the $\eta^2$-$S_2R$ ligand functioning as a formal three-electron donor to the tungsten center [W–S = 2.479 (2) and 2.453 (3) Å]. The solid-state molecular structure of **8a** is probably similar to that of the related 16-electron monomer $CpMo(NO)(SPh)_2$,[47] for which Mo–S multiple bonding has also been invoked.



(12)

The spectroscopic properties of complexes **6**–**8** (presented in Tables I and III) are consistent with their retaining their monomeric molecular structures (Scheme I) in various solutions. Particularly noteworthy properties are the following:

(1) solutions of all five complexes exhibit a single, strong $\nu_{NO}$ in the IR region of 1647–1599 $cm^{-1}$ characteristic of a terminal nitrosyl ligand. These $\nu_{NO}$'s and that of the parent **2** are indicators of the relative electron density at the metal centers in the various compounds and suggest that the net electron-donating abilities of the alkyl-containing ligands decrease in the order R > $\eta^2$-$S_2R$ > ER (R = $CH_2SiMe_3$; E = S or Se).

(2) In addition to one Cp resonance, the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **6a**, **6b**, and **7** contain two sets of signals for their two different alkyl groups whereas **8a** and **8b** show only one set, thereby indicating that the alkyl groups within each are equivalent.

(3) The diasterotopic methylene protons of the $CH_2SiMe_3$ groups in complexes **6**–**8** give rise to the appropriate AB quartets in the respective $^1H$ NMR spectra of the compounds in $C_6D_6$. Furthermore, the $^1H$ and $^{13}C\{^1H\}$ NMR signals due to the metal-bound methylenes in complexes **6a**, **6b**, and **7** also display the expected $^{183}W$ satellites. Interestingly, the resonance due to the $CH_2$ carbon bound to W in 18-electron **7** appears at a significantly higher field ($\delta$ −3.22) than the corresponding resonances of 16-electron **6a** ($\delta$ 32.71) and **6b** ($\delta$ 37.57) and is more reminiscent of the analogous signals of 18-electron **4a** ($\delta$ −8.12) and **4b** ($\delta$ −7.18).

(4) $^1H$ NMR spectra of **6a** or **6b** in $C_6D_5CD_3$ at −35 °C reveal the existence of two isomers for each complex in this solution, and magnetization transfer studies demonstrate that the two isomers are interconverting. These isomers probably result from inversion at the sulfur or selenium atoms of the $ECH_2SiMe_3$ ligands (E = S or Se) in **6a** or **6b**. Consistent with this view is the fact that in the ambient-temperature $^1H$ NMR spectrum of both complexes in $C_6D_6$, the signals due to the alkyl group attached to the S or Se atom are broader than those attributable to the alkyl group directly bonded to W. Similar inversion processes have been well documented for S- and Se-containing derivatives of group 6 carbonyls.[48] Nevertheless, no evidence for the occurrence of such inversion processes is readily apparent in the spectroscopic properties of **8a** or **8b**.

Information concerning the insertion of elemental sulfur and selenium into metal–carbon $\sigma$-bonds is still quite ru-

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[43] Middleton, A. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1981**, 1898 and references cited therein.

[44] (a) Wailes, P. C.; Weigold, H.; Bell, A. P. *J. Organomet. Chem.* **1972**, *34*, 135. (b) Fochi, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1986**, 445.

[45] Evans, S. V.; Legzdins, P.; Rettig, S. J.; Sânchez, L.; Trotter, J., manuscript in preparation.

[46] At present, there is not even spectroscopic evidence for the existence of $CpW(NO)(CH_2SiMe_3)(\eta^2$-$Se_2CH_2SiMe_3)$, the selenium congener of **7**.

[47] Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730.

[48] Abel, E. W.; Bhargava, S. K.; Orrell, K. G. *Prog. Inorg. Chem.* **1984**, *32*, 1 and references cited therein.

dimentary since only a small number of papers dealing with this subject has appeared to date.[13b,49] Without question, the sequential transformations shown in eq 12 constitute the first documented examples of this type of reactivity. Hence, the mechanisms operative during these conversions are of fundamental interest and significance. We have previously proposed[13b] that the first two sulfur-insertion steps involve initial coordination of $S_8$ as a nucleophile to a formally 16-electron tungsten center followed by intramolecular migratory insertion into the W–$CH_2SiMe_3$ or W–$SCH_2SiMe_3$ linkages, respectively. This view has gained some acceptance in the interim.[50] Regrettably, however, we have so far been thwarted in our attempts to obtain reliable kinetic data for either of the first two steps of reaction 12 when E = S (i.e. the conversions **2a** → **6a** and **6a** → **7** of Scheme I).[51] As outlined in the Experimental Section, these reactions are best effected on a preparative scale under heterogeneous conditions with the sulfur incompletely dissolved in toluene. When effected under homogeneous conditions during attempted kinetic analyses, both conversions require longer periods of time (weeks) to proceed to completion in toluene. Furthermore, the rates of the homogeneous reactions are markedly accelerated by trace amounts of water. Hence, it may well be that the mechanisms of sulfur and selenium insertion into these M–C bonds are more complex than we originally envisaged.

## Summary

This work has demonstrated that unusual 16-electron, dialkyl nitrosyl complexes of molybdenum and tungsten, $CpM(NO)R_2$, may be conveniently synthesized by sequential reaction of the diiodo dimers $[CpM(NO)I_2]_2$ with the corresponding bulky Grignard reagent, RMgX, and then $H_2O$. The formulation of the dialkyl products as monomeric entities having three-legged piano-stool molecular structures has been confirmed by a single-crystal X-ray crystallographic analysis of $CpW(NO)(CH_2SiMe_3)_2$. Evidently, the coordinatively unsaturated $CpM(NO)R_2$ compounds owe their relative thermal stability to a combination of steric and electronic factors[52] which effectively impede the traversal of possible decomposition pathways. For instance, the absence of β-hydrogens in the alkyl ligands precludes β-H elimination.

Studies of the chemistry of $CpW(NO)(CH_2SiMe_3)_2$ as a prototypal member of this series of compounds have led to three important conclusions concerning its reactivity, namely, (a) strong Lewis acids such as $AlMe_3$ add to the oxygen atom of its nitrosyl ligand, but the resulting isonitrosyl linkage is easily cleaved by water, (b) small, strong Lewis bases such as $PMe_3$, bind to the tungsten center, but this binding is not sufficiently strong to withstand exposure of the adduct to vacuum, and (c) other donor molecules such as $O_2$, CO, CNR′, NO, $Se_8$, $S_8$, etc. also presumably coordinate initially to the metal center, but, most importantly, then undergo subsequent intramolecular transformations involving the alkyl ligands (as summarized in Scheme I). These chemical properties of $CpW(NO)(CH_2SiMe_3)_2$ contrast with those exhibited by the analogous 18-electron $Cp'M(NO)R_2$ derivatives of iron and ruthenium.[7,8] The latter, coordinatively saturated complexes are prone to undergo reductive elimination of the alkyl ligands or to effect migratory insertion of the bound NO into their metal–carbon bonds. No evidence for this kind of reactivity has yet been found for the 16-electron tungsten dialkyl compound. Rather, the chemistry of $CpW(NO)(CH_2SiMe_3)_2$ resembles that found for other coordinatively unsaturated compounds of group 6 metals such as $W(CO)(PR_3)_2$ and $Mo(diphos)_2(CO)$ which also have the capacity to incorporate donor molecules.[38] Nevertheless, the presence of the alkyl ligands in the former compound enables it to traverse subsequent reaction paths that are simply not accessible to the carbonyl phosphine species, e.g. insertion of the incoming donor molecule into a tungsten–carbon bond (Scheme I). In this latter sense, there are some similarities of the chemistry of $CpW(NO)(CH_2SiMe_3)_2$ to that exhibited by the 16-electron $Cp'_2MR_2$ derivatives of the group 4 metals.[44,53] However, there are also some striking differences, most notably the reactions of the tungsten dialkyl with elemental oxygen and sulfur.

Studies directed at (a) synthesizing other $CpM(NO)R_2$ complexes with less sterically demanding R groups, (b) establishing the mechanisms of their unique transformations, and (c) asertaining the utility of this unique class of compounds in organic syntheses are currently in progress.

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**Registry No.** **1a**, 116232-35-0; **1a**·$Et_2O$, 116263-26-4; **1b**, 116232-36-1; **1b**·$Et_2O$, 116232-37-2; **2a**, 94620-67-4; **2b**, 94620-69-6; **2c**, 94620-68-5; **2d**, 116232-38-3; **2e**, 116232-39-4; **3**, 116232-40-7; **4a**, 116232-41-8; **4b**, 116232-42-9; **5**, 116232-43-0; **6a**, 97920-55-3; **6b**, 116232-44-1; **7**, 97920-56-4; **8a**, 97920-57-5; **8b**, 116232-45-2; $[CpW(NO)I_2]_2$, 71341-43-0; $Me_3SiCH_2MgCl$, 13170-43-9; $[CpMo(NO)I_2]_2$, 12203-25-7; $Me_3CCH_2MgCl$, 13132-23-5; $PhCMe_2CH_2MgCl$, 35293-35-7; $PhCH_2MgCl$, 6921-34-2; *t*-BuNC, 7188-38-7; S, 7704-34-9; Se, 7782-49-2.

**Supplementary Material Available:** Tabulations of the calculated hydrogen parameters, anisotropic thermal parameters, and torsion angles for $CpW(NO)(CH_2SiMe_3)_2$ (3 pages); a listing of structure factor amplitudes for $CpW(NO)(CH_2SiMe_3)_2$ (25 pages). Ordering information is given on any current masthead page.

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